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Chemical Analysis Procedures for Forest Fire Retardant Constituents

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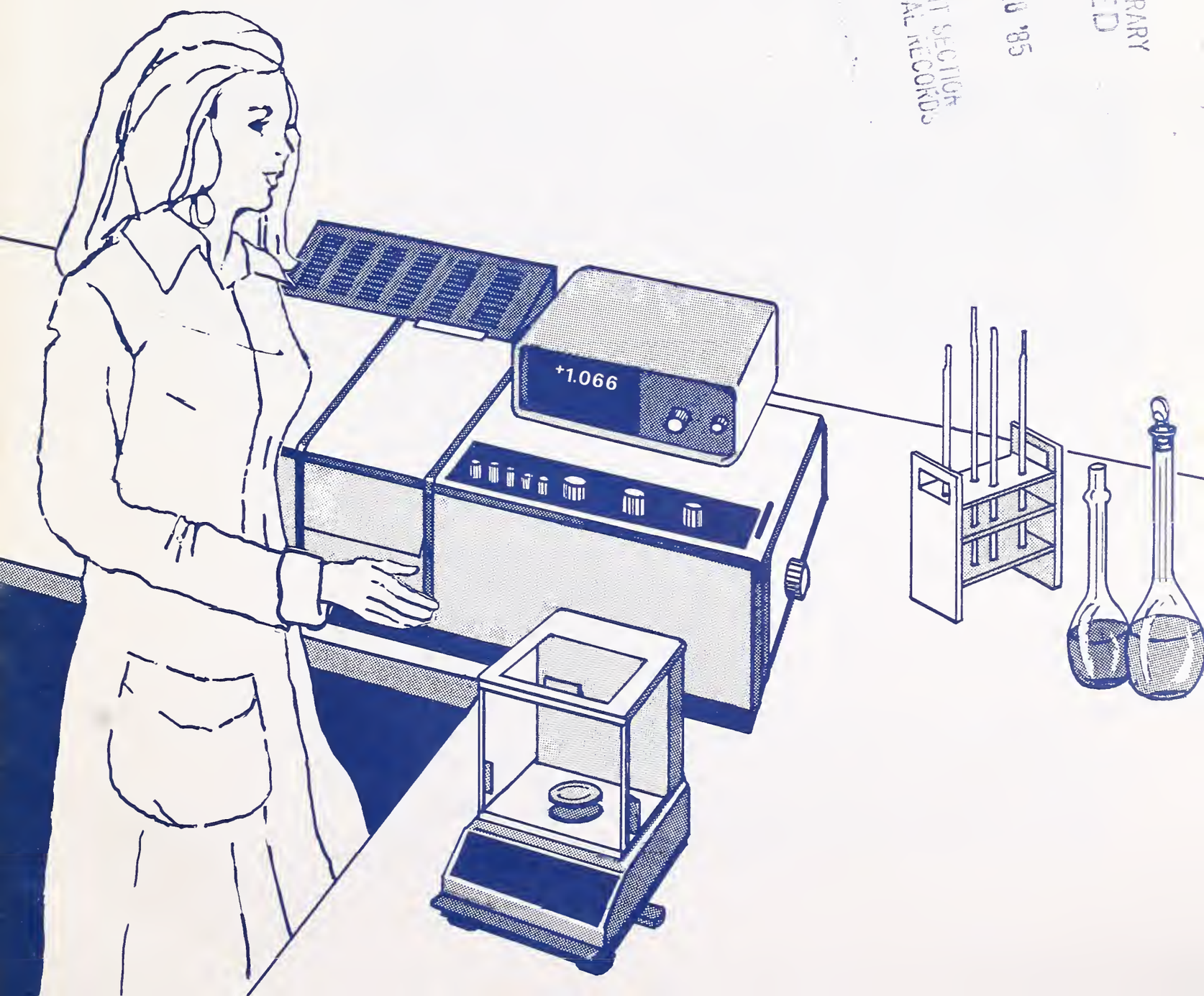

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RESEARCH SUMMARY

The report describes chemical analysis procedures developed and/or in use at the Intermountain Fire Sciences Laboratory to determine the quantitative composition of fire retardant mixtures. These mixtures contain inorganic salts, coloring agents, and inhibitors of spoilage and corrosion. Among them are phosphate, sulfate, iron, acracid red 73 dye, 2-mercaptobenzothiazole, dichromate, thiosulfate, ferrocyanide, and thiocyanate. A procedure is also given for measuring field application rates (gallons/100 ft^2) by determining the amount of a salt component on a known area of vegetation/soil/duff.

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INTRODUCTION

Wildland fire retardant mixtures used for aerial (and sometimes ground) application contain, in addition to water, several categories of constituents. Certain salts are used to give long-term retardant capability, that is, effectiveness is retained after the water has evaporated. These include ammonium dihydrogen phosphate (MAP), diammonium hydrogen phosphate (DAP), ammonium polyphosphates (APP), and ammonium sulfate. Proprietary blends of the phosphates and sulfates are also used. Most retardants are thickened by adding some type of clay or one of several kinds of polymeric organic compounds, natural or synthetic. Usually a coloring agent is used, such as iron oxide or a synthetic dye. When organic polymers are present, a spoilage inhibitor is usually added to control molds, fungi, and bacteria. In most cases, substances are added that minimize the rate of corrosion of metal parts of the handling or transporting equipment.

In the course of conducting research, chemical procedures have been developed for measuring quantitatively the concentrations of many of these components. Based on these analyses, simple field test methods for determining salt content have been devised and calibration tables developed relating properties such as specific gravity to the actual retardant salt content. Although such field procedures have been developed and are being used operationally, there is often a need to analyze for specific fire retardant ingredients. In most of the specific analyses, the fundamental method is not new, but specific conditions, operations, and procedures have been developed to yield optimum results with normal mixtures of ingredients present in fire retardants.

There is an increasing need to determine the concentration of various retardant ingredients as well as the level of retardant coverage in specific laboratory and field research or administrative studies.

The detailed analytical procedures in this report have been used successfully, and each is the result of refinement through experience over several seasons of use.

In some cases, depending on the specific combinations of chemicals in a product, a calibration curve may be needed. This happens when one chemical is partly absorbed onto another, chemicals within a product react so that they are not detected, or the same ion may be present from several sources. The result is an inability to detect the proper amount of chemical even when a suitable procedure is used, unless a correction factor is incorporated in some manner, such as a calibration curve.

ACTIVE RETARDANT SALTS

Most long-term fire retardants (those that are effective after the moisture has been evaporated) are composed of either monoammonium phosphate, diammonium phosphate, ammonium polyphosphate, or diammonium sulfate. Because the combustion-retarding effectiveness of long-term fire retardants is related to the concentration of these active salts, their accurate determination is essential. In some situations an adequate analysis can be obtained by determining the ammonia nitrogen content. This is possible because all presently used active retardant salts contain ammonia in specific ratios of nitrogen to the fire retardant anion (phosphate or sulfate). The ammonia, however, is not essential in the combustion altering process and does not assure a measure of effectiveness as does the phosphate or sulfate. This section describes procedures to analyze fire retardant mixtures for ammonia nitrogen, inorganic orthophosphate and polyphosphate, and sulfate.

Determination of Ammonia Nitrogen (Kjeldahl Method)[1]

This method can be used as a direct measure of nitrogen present as ammonia and as an indirect determination of the active salt when it is present in known proportions as is the case with mono- or diammonium phosphate and diammonium sulfate. It is possible for nitrogen, sulfate, and phosphate to be present from other sources. Therefore, this method may be slightly less accurate than the direct methods unless an appropriate adjustment is made. Usually the composition of the retardant is well known, and because it is relatively simple and fast, the Kjeldahl method will often be preferred.

I. Preparation of Solutions

A. NaOH, 40 percent.—Gradually add 40 g of NaOH pellets to 60 g of distilled water with stirring (a magnetic stirrer is preferable because dissolution is slow). Use extreme caution; a large quantity of heat is evolved when NaOH is dissolved and the concentrated solution is extremely caustic.

B. Boric acid solution, 2 percent.—Add 2 g of boric acid crystals to 98 g of distilled water with stirring.

C. Sodium hydroxide, 0.02 N.—Dissolve 0.8 g of NaOH pellets in approximately 500 mL of distilled water in a 1-liter volumetric flask. Add distilled water to the mark and mix well. Standardize against potassium acid phthalate.

D. Hydrochloric acid, 0.02 N.—Carefully add 1.7 mL of concentrated hydrochloric acid to approximately 500 mL of distilled water in a 1-liter volumetric flask. Dilute to mark and mix well. Standardize the acid using standard 0.02 N sodium hydroxide.

E. Bromocresol green - methyl red mixed indicator.

1. Bromocresol green.—Dissolve 0.2 g bromocresol green in 14.3 mL of 0.01 N sodium hydroxide in 250 mL volumetric flask. Dilute to mark with distilled water.

2. Methyl red.—Dissolve 0.1 g methyl red in 150 mL of ethanol in 250 mL volumetric flask. Dilute to mark with distilled water.

3. Pour equal volumes of the two indicator solutions together and store in a stoppered bottle.

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[1]American Public Health Association; American Water Works Association; Water Pollution Control Federation. Standard methods for the examination of water and wastewater. 14th ed. Washington, DC; 1976: 417-418.

II. Standardization of Titrants

A. Sodium hydroxide, 0.02 N.

1. Dry about 5 g of potassium acid phthalate (KHP) primary standard for about 1 hour at 100 °C. Cool in dessicator. Weigh exactly, approximately 1 g of dried KHP into 250-mL volumetric flask. Dissolve in about 100 mL of boiled, cooled distilled water. Fill to mark with additional boiled, cooled distilled water. Calculate the normality of the KHP by:

$$VN = \frac{\text{weight}}{MW_{KPH} / H^+ \text{ equivalent}}$$

where

V = volume of solution, in liters = 0.25
N = normality of the solution
MW = molecular weight of KHP = 204.23
H^+ equivalent = 1
Weight = sample weight in grams.

Substituting:

$$N = \frac{\text{wt sample}}{51.06}$$

2. Pipet 5 mL of NaOH solution into a 50-mL Erlenmeyer flask. Add 3 drops of mixed indicator and about 5 mL of distilled water to the flask. Titrate with the KHP solution to a faint pink color. Perform at least 3 replicates. Determine the normality of the NaOH by:

$$(VN)_{acid} = (VN)_{base}$$

B. Hydrochloric acid 0.02 N.—Repeat procedures in step II.A.2, substituting the unknown hydrochloric acid for the KHP and titrate. Determine the normality of the acid from the volumes used and the normality of the base previously determined.

III. Distillation of Ammonia

A. If the distillation apparatus has not been used recently, clean the boiling chamber thoroughly and distill about 30 mL of water to remove any residue. Discard the distillate.

B. Weigh to 0.1 mg about 0.07-0.10 g of mixed retardant in a small beaker, and add 2 to 3 mL distilled water. Transfer sample to the preheated boiling chamber. Rinse beaker twice with about 2 mL of distilled water and add to the reaction flask.

C. Add 10 mL of 40 percent NaOH being careful to avoid suckback of boric acid.

D. Collect the liberated ammonia in 10 mL of 2 percent boric acid. The tip of the condenser must be immersed in the boric acid during NaOH addition and throughout the distillation.

E. Continue distillation until 25 mL of distillate have been collected.

F. Add 3 drops of mixed indicator to the distillate and titrate with 0.02 N HCl to a faint pink color.

G. Rinse entire assembly with distilled water and flush to remove remaining sample and traces of NaOH.

H. Perform at least three replicate distillations and titrations.

I. Calculate the amount of nitrogen as follows:

$$\%\text{nitrogen} = \frac{(V)(N)(14.007)}{10\ (wt)}$$

where

V = volume of HCl in mL

N = normality of HCl

wt = sample mass in g.

For indirect determination of salt: the above equation may be modified, based on known ratios of nitrogen to phosphate or sulfate:

Ammonium Sulfate or Diammonium Phosphate:

$$\%\text{salt} = \frac{(V)(N)(132.1)}{20\ (\text{wt})}$$

Monoammonium Phosphate:

$$\%\text{salt} = \frac{(V)(N)(115.03)}{10\ (\text{wt})}$$

Ammonium polyphosphate[2] (of the form X-Y-O where X is amount of N and Y is the amount of P_2O_5):

$$\%\text{salt} = \frac{(V)(N)(14.008)(Y/X)}{10\ (\text{wt})}$$

Colorimetric Determination of Inorganic Orthophosphate and Polyphosphate[3]

The detection of phosphate by this method is very sensitive. In a laboratory where retardants are routinely handled in large amounts, stray dust is a primary hazard through its settling on all available surfaces and thereby contaminating utensils and glassware. Extreme care is necessary to achieve and maintain "clean" vessels. Failure to do this will cause inaccurate blanks and poor reproducibility in all readings.

I. Preparation of Reagents

A. Ammonium molybdate-perchloric acid solution (AMPA).— Dissolve 12.5 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\bullet 4H_2O$, in 250 mL of distilled water in a 500-mL Erlenmeyer flask. Measure 25.0 mL of 72 percent perchloric acid (CP) in a graduated cylinder and add it **slowly** to the molybdate solution, with swirling. Cover with an inverted beaker. Store overnight; then filter the solution to remove crystals.

B. Amino-napthol-sulfonic acid solution (ANSA).—Into a 250-mL volumetric flask, weigh 0.500 g 1-amino-2-napthol-4-sulfonic acid, 30.0 g sodium bisulfite ($NaHSO_3$ CP), and 6.0 g sodium sulfite (Na_2SO_3 CP). Add distilled water to dissolve; then fill to mark. Store overnight; then filter the solution to remove crystals.

C. Refrigerate both solutions after filtration, storing the ANSA solution in an amber or dark-colored bottle. Prepare fresh solutions at least every 2 weeks.

II. Preparation of the Standard Curve

A. Into a 50-mL Erlenmeyer flask, weigh 0.3835 g monobasic potassium phosphate (KH_2PO_4). Add 20 mL distilled water and 1 mL concentrated HCl (CP). On a hot plate, heat to a boil; then cool. Wash the contents of the

[2]This is a less accurate determination because exact ratios of N to P are not established.

[3]American Society for Testing and Materials. Annual book of ASTM standards, part 31: Water. Philadelphia, PA; 1976: 392-394.

flask into a 1-liter volumetric flask and fill to the mark. Mix thoroughly. This solution contains phosphorus equivalent to 200 ppm P_2O_5 (200 mg P_2O_5/liter).

B. Prepare standard solutions. Adding the following volumes of the 200-ppm standard to successive 250-mL volumetric flasks, and diluting to the marks, create the following solutions:

1 mL (200 ppm) in 250-mL vol. flask = 0.80 ppm P_2O_5
3 mL (200 ppm) in 250-mL vol. flask = 2.40 ppm P_2O_5
5 mL (200 ppm) in 250-mL vol. flask = 4.00 ppm P_2O_5
10 mL (200 ppm) in 250-mL vol. flask = 8.00 ppm P_2O_5
15 mL (200 ppm) in 250-mL vol. flask = 12.00 ppm P_2O_5
20 mL (200 ppm) in 250-mL vol. flask = 16.00 ppm P_2O_5
25 mL (200 ppm) in 250-mL vol. flask = 20.00 ppm P_2O_5

C. Pipet 25.0 mL of each of the above solutions into 50-mL Erlenmeyer flasks or other suitable Pyrex-type containers. Prepare reagent blanks consisting of 25.0 mL of distilled water to be tested at the same time. This must be done in groups of 2 or 3, so that time for filling and rinsing spectrometer cells is allowed for within the reaction time constraint of part E, below.

D. Add 4.0 mL of the AMPA solution to each flask. Mix well. The perchloric acid of this solution, in the absence of much acid or base in the standard (or later, in analysis samples) produces a pH in the range 1.0 to 1.2. This is necessary for the color development to follow.

E. Add 2.0 mL of the ANSA solution to each sample. Allow color to develop for 10 minutes. This is fairly critical; the absorbance should be measured within ±½ minute of the 10-minute mark. Space the ANSA additions at about 3-minute intervals. Set a UV-visible spectrometer at 700 nm wavelength, and use 1-cm plastic or glass cells; distilled water serves as the blank.

F. Repeat measurements on one or more standard solutions after each half-dozen or so analytical samples have been run. The range of absorbance values for any one standard during a typical work period (a half day) should not be more than about 0.01 absorbance unit.

G. Interpretation of the absorbance values of analysis samples can be done manually using graph paper, or by a computer program. The standard sample data yield a straight line.

III. Analyzing Retardant Samples

A. Accurately weigh about 0.100 g of the liquid retardant sample into a 100-mL volumetric flask. Dilute to the mark with distilled water. Mix well. Remove a 10-mL aliquot of this solution and transfer to a second 100-mL volumetric flask. Dilute to the mark and mix well. With ordinary mixed retardant samples, the second solution should produce absorbance values on the linear portion of the standard curve. Retardant concentrates may require additional dilution.

B. Prepare triplicate (or duplicate) samples using the procedure in part III.A.

C. Using the final solution flasks prepared above, pipet 25 mL of each solution to a 50-mL Erlenmeyer flask or other suitable Pyrex-type container.

D. Using the procedure outlined in parts II.C, D, and E, record the absorbance values, subtract the absorbance of the reagent blank from the sample absorbance, and, using the standard curve or computer, record the corresponding concentration, ppm P_2O_5.

E. Calculate the percent P_2O_5 in the original sample using the following formula:

$$\%P_2O_5 = \frac{(0.100)\ \text{concentration from standard curve, ppm } P_2O_5}{\text{mass sample, grams}}$$

Each retardant analyzed will have triplicate (or duplicate) results, which should be averaged for the final $\%P_2O_5$ report.

IV. Analyzing Retardant Samples Containing Polyphosphate

If the retardant contains polyphosphate species (usually present in "liquid concentrate" sources of phosphate), the polymeric bonds must be hydrolyzed before the determination step in II.E.

A. Prepare stocks of 5.2 N H_2SO_4 and 5.0 N NH_4OH. These must be tested to verify that they are free of phosphate, or blanks must be run to determine a correction factor.

B. Follow the dilution steps of part III.A.

C. Pipet 25.0 mL samples of the diluted retardant into 50 mL Erlenmeyer flasks. Add 2.00 mL of the H_2SO_4 to each one. Add a few chips of broken glass and boil gently for 30 minutes. Such chips avoid the potential for cross-contamination posed by porous chips. Add distilled water to maintain volumes of not less than 10 mL. After cooling, add 2.00 mL of the NH_4OH and dilute to about 20 mL.

D. Measure the pH and add more 5.2 N acid or 5.0 N base if the pH is outside the range 1.0-1.2. Transfer to a graduated cylinder and bring the volume up to 25.0 mL.

E. Pour solution into a 50 mL Erlenmeyer flask and proceed to parts II.D and E.

V. Notes

A. "CP" (chemically pure) chemicals should be used throughout this procedure. Refer to the manufacturers' analyses for determination of phosphorus levels, which may interfere with this procedure. Questionable chemicals should be analyzed for phosphorus content, using the procedure outlined for fire retardant analysis, since these chemicals can cause artificially high phosphate levels unless a blank is run.

B. Mixing solutions in volumetric flasks is most thoroughly accomplished by inverting the stoppered flask and swirling it gently, repeating this 25 times.

C. Care must be used with perchloric acid because it may generate potentially explosive materials when it comes in contact with organic compounds.

D. One or two standard solutions analyzed with each batch of retardant samples provide a quality-control of reagents and procedures. Reference to the standard curve plot will show if drifting is occurring. This may indicate deterioration or contamination of reagents.

E. Because of volume changes when solids go into solution, it is important not to fill the volumetric flasks to the mark until all solids are completely dissolved.

F. Conventionally cleaned glassware (with phosphate-free detergent) should be rinsed with hot 3 M HCl solution (at least 60 °C), followed by at least four rinses with distilled water. Glassware should be stored in a clean, closed cabinet and should be either inverted or sealed with Parafilm. It is convenient to store pipets in plastic bags. When stored for more than a couple of days, glassware should be covered entirely (a closed cabinet or an overlay of paper or plastic sheet).

Colorimetric Determination of Sulfate[4]

The determination depends on the formation of a colored complex between barium ions (Ba^{+2}) and methylthymol blue (MTB). A solution containing MTB and barium chloride in a solution at low pH (2.5-3.0) is added to the sample. Some $BaSO_4$ precipitates; then when the pH is raised (to 12.5-13.0), the excess Ba^{+2} reacts with the reagent. The absorbance is measured at about 620 nm. The region 650 to 600 nm should be scanned because other components of retardants sometimes shift the wavelength of maximum absorbance.

The concentration of sulfate is proportional to the **decrease** in absorbance between the blank and the sample. A standard curve must be prepared since the relation is not strictly linear.

Fresh solutions of diluted standard sulfate and MTB-Ba^{+2} must be prepared daily. A stock standard solution of K_2SO_4 at 0.0100 mole per liter and the $BaCl_2$ standard solution can be stored.

I. Preparation of Reagents

A. Standard sulfate solutions.—Dissolve 0.1743 g of anhydrous K_2SO_4 in distilled water and dilute it to 100.0 mL. This solution is 0.0100 M in SO_4^{-2}. Prepare a series of standards by dilution as follows:

2.00 mL of 0.0100 M SO_4^{-2} to 250 mL = 8.0×10^{-5} M SO_4^{-2}
1.50 mL of 0.0100 M SO_4^{-2} to 250 mL = 6.0×10^{-5} M SO_4^{-2}
50.0 mL of 8.0×10^{-5} M SO_4^{-2} to 100 mL = 4.0×10^{-5} M SO_4^{-2}
25.0 mL of 8.0×10^{-5} M SO_4^{-2} to 100 mL = 2.0×10^{-5} M SO_4^{-2}
25.0 mL of 4.0×10^{-5} M SO_4^{-2} to 100 mL = 1.0×10^{-5} M SO_4^{-2}

B. Standard barium chloride solution.—Dissolve 0.1526 g of $BaCl_2 \cdot 2H_2O$ in distilled water; transfer the solution to a 100-mL volumetric flask; dilute to the mark and mix. This solution is 0.006247 M in Ba^{+2}.

C. Acid and base solutions.—Prepare a stock solution of 0.10 M HCl. Prepare a stock solution of 0.20 M NaOH.

D. MTB reagent solution.—Weigh 0.0118 g of MTB into a 100-mL beaker. Add about 15 mL of methanol and stir carefully until all grains of solid have dissolved. Transfer the solution to a 100-mL volumetric flask using several small portions of methanol and being very careful to avoid losing reagent through "creep" of the solution and evaporation of solvent. Add 2.50 mL of the $BaCl_2$ standard solution, 4.0 mL of 0.10 M hydrochloric acid, and 7.1 mL of distilled water. Dilute to the mark with methanol and mix.

II. Preparation of Sample

Weigh about 25 g (±0.01 g) of the retardant into a 100-mL beaker, add distilled water to dilute and suspend the material; then transfer it quantitatively into a 250-mL volumetric flask. Fill to the mark and mix the solution; centrifuge a portion of it to remove solids.

Make two successive dilutions of the supernate. For the first, dilute 5.00 mL to 250.0 mL. For the second, dilute 5.00 mL of the first diluted solution to 200.0 mL. This gives an overall dilution factor of 2,000. The resulting solution is ready for colorimetric analysis.

III. Determination Step

A. Pipet 5.00 mL of a diluted sulfate standard solution or of a retardant sample solution into a 50-mL volumetric flask. (The size and shape are convenient; the whole volume will not be used.)

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[4]McSwain, Michael R.; Watrous, Russel J.; Douglass, James E. Improved methylthymol blue procedure for automated sulfate determinations. Anal. Chem. 46(9): 1329; 1974.

B. Add 3.5 mL of methanol and 3.5 mL of the MTB reagent solution (step I.D). Stopper the flask and shake for about 30 seconds.

C. Add 1.0 mL of 0.20 M NaOH and shake for another 30 seconds.

D. Immediately transfer some of the solution to a cuvette and measure the absorbance at about 620 nm. (Scan enough to read the maximum absorbance.) Repeat the above steps for each standard, each sample, and a blank (5.00 mL of distilled water).

IV. Calculations

A. Tabulate absorbances for the standard and retardant samples, subtracting the absorbance of the blank from each.

B. Plot the standard absorbances against the corresponding sulfate concentrations; draw the best smooth curve through the points.

C. For each retardant sample, read off a sulfate molarity from the curve.

D. For each retardant sample, calculate the ammonium sulfate concentration:

$$\%(NH_4)_2SO_4 = (\text{sulfate molarity}) \frac{6.61 \times 10^6}{\text{grams sample}}$$

Note: Consistent timing at each step is critical for reproducible results.

Turbidimetric Determination of Sulfate[5]

The measurement step utilizes the light-scattering property of a suspension of barium sulfate. As a convenience, the Hach SulfaVer® IV reagent "pillows" are used to add the precipitating chemicals. It is important that the precipitating reaction be allowed to proceed for at least 5 but not more than 10 minutes.

I. Preparation of Standard Solutions

A. Weigh 0.3697 g of anhydrous, reagent grade Na_2SO_4. Dissolve it in distilled water and transfer the solution quantitatively into a 500-mL volumetric flask. Fill the flask to the mark and mix. This yields a 500-ppm solution (as SO_4^{-2} ion).

B. Make dilutions of the 500-ppm solution to make the following standards. Use volumetric pipets or a buret, and 100-mL volumetric flasks.

Desired concentration	**Volume 500 ppm**
ppm	*mL*
10	2.00
20	4.00
40	8.00
60	12.00
80	16.00

II. Processing Retardant Samples

A. Weigh to ±0.001 g about 1.0 g of mixed retardant into a 1-liter volumetric flask, add about 100 mL distilled water, and swirl until the sample is dispersed; then fill to the mark and mix.

B. If the coloring agent or thickener is not totally water soluble, centrifuge a portion large enough to provide a 25-mL aliquot of clear solution.

C. Pipet 25.00 mL of the clear solution into a 100-mL volumetric flask, dilute to the mark, and mix. This solution is ready for the determination step.

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[5]American Public Health Association; American Water Works Association; Water Polution Control Federation. Standard methods for the examination of water and wastewater. 14th ed. Washington, DC; 1976: 496-498.

III. Turbidimetric Measurement

A. If the sample solution is not water-clear, for any reason, some of solution from step II.C must be used as a blank. Its absorbance must be subtracted from each measurement of sample turbidity.

B. For each measurement, standard, or unknown, use the following procedure:

1. Set the wavelength to 450 nm (or set up to scan over that wavelength).
2. Pipet 25.00 mL of solution into a glass-stoppered 50-mL graduated cylinder.
3. Add the contents of one SulfaVer IV packet to the cylinder; stopper, and invert at least six times. Start a 5-minute timer.
4. Fill the instrument cuvette with distilled water and confirm a zero-absorbance reading.
5. After 5 minutes, rinse the cuvette three times with the turbid sample, fill it, and measure the absorbance.

IV. Computations

A. Plot the absorbance (vertical) against concentration (horizontal) for the standard solutions. Using a French curve, draw a smooth curve through the points.

B. From the absorbance of the unknown(s), read off corresponding concentrations. (Subtract absorbance due to color first, if that is necessary.)

C. Calculate the composition of the retardant:

$$\text{Wt\%}(NH_4)_2SO_4 = (0.5503)\ \frac{\text{concentration ppm}}{\text{sample mass}}$$

FIRE RETARDANT COLORING AGENTS

Nearly all fire retardants contain a coloring agent. These substances, which may be water soluble dyes or insoluble pigments such as iron oxide, are added to enable firefighting personnel, especially air attack officers and airtanker pilots, to see where retardant has been applied. This is necessary to obtain continuous lines of retardant when more than one pass or load is needed to provide the desired concentration, width, or length. While color is less important for ground-applied retardants, it is often convenient to be able to see where retardant has been applied. Color is also frequently used to estimate the amount of retardant applied. This section describes the analysis procedures used to determine quantities of iron oxide and several commonly used dyes.

Atomic Absorption Determination of Iron[6]

Iron oxide (Fe_2O_3) is the most common coloring agent used in fire retardants. It is normally very finely ground and, because it is insoluble, held in suspension by a thickening agent. In this analysis the oxide is dissolved in hydrochloric acid, followed by determination of the Fe^{+3} concentration by atomic absorption spectroscopy. All analyte solutions are 1 percent (V/V) in HCl (approximately 0.12 M), and the expected range of iron concentrations is between 1 and 5 ppm (as Fe^{+3}).

I. Standard Iron Solutions

Pipet 5.00 mL of the 1,000-ppm stock solution into a 100-mL volumetric flask. Add distilled water to the mark and mix the solution. The resultant solution

[6]Perkin-Elmer Manual. Analytical methods for AA (0993-8039), Perkin-Elmer Corporation, Norwalk, CT; 1982.

contains 50.00 ppm of Fe^{+3}. Prepare standards by diluting portions of the 50-ppm solution, adding HCl as needed. Examples (each diluted to 100 mL):

Desired concentration	Volume, 50 ppm	Volume concentration HCl
ppm	*mL*	*mL*
1.0	2.00	1.00
2.0	4.00	1.00
5.0	10.00	1.00

II. Preparation of Sample

A. Retardants that do not contain ferrocyanide.—Weigh accurately about 2.5 g of the mixed retardant into a small Erlenmeyer flask. Add about 2 mL distilled water and 10 mL concentrated hydrochloric acid. Warm the mixture on a hot plate until the red color (opaque) changes to a clear, yellow solution. Transfer the solution quantitatively into a 1-liter volumetric flask, dilute to the mark, and mix well.

B. Retardants that contain ferrocyanide.—For samples that contain ferrocyanide, the formation of Prussian blue must be avoided. Nitric acid will decompose the ferrocyanide and oxidize the iron to Fe^{+3}. Weigh the sample into a 100-mL beaker (instead of the Erlenmeyer flask). Add 5 mL of concentrated nitric acid and heat the mixture on a hot plate with frequent swirling until most of the acid has evaporated; then add 10 mL concentrated hydrochloric acid and proceed to the last half of the previous paragraph.

C. Retardants that contain clay.—In the case of clay-thickened materials, a colorless turbidity will remain after the hot-acid digestion. Weigh the sample into a small Erlenmeyer flask; add 2 mL distilled water and 10 mL concentrated HCl. Warm the mixture until the color changes from the red of the iron oxide to the yellow of the Fe^{+3} ion in chloride solution. Centrifuge this mixture to obtain a clear solution. After transferring the clear solution to a 1-liter volumetric flask, using a transfer pipet or dropper, wash the solids once with distilled water. Add the wash water to the rest of the liquid, dilute to the mark, and mix.

III. Determination Step

Using techniques appropriate to the AA spectrometer available, determine the Fe^{+3} concentration in the final sample solution.

IV. Calculation

$$\%Fe_2O_3 = (\text{conc.,ppm}) \frac{0.1430}{\text{grams sample}}$$

Colorimetric Determination of Acracid Red 73 Dye[7]

This procedure is appropriate for any retardant material that is a clear solution or that contains suspended solids that can be removed by settling, centrifugation, or filtration and uses acracid red 73 dye as a coloring agent. The clarified sample is diluted with water and the light absorbance is measured at 510 nm wavelength. The method is applicable to any retardant containing acracid red 73. The calculation will need to be modified for other materials.

I. Preparation of a Standard Sample of the Retardant for which the Analysis is to be Conducted

[7]Developed by the staff of the Intermountain Fire Sciences Laboratory based on known chemical properties of the analyte substance.

A. Combine the retardant ingredients[8] in a small blender.

B. Blend the mixture 15 minutes at high speed.

C. Dilute 5.00 g of the mixture with distilled water to a total volume of 25.0 mL, stir it well; then centrifuge it to separate solids.

II. Preparation of a Standard Curve

A. Dilute aliquot volumes of the clear supernate obtained in section I.C, above, in 100-mL volumetric flasks. Use aliquots of 0.25, 0.50, 0.75, 1.00, and 1.25 mL.

B. Measure the absorbance at 510 nm of each of the diluted aliquots.

C. Plot a graph, absorbance (vertical) against concentration of the dye in the 100-mL analysis solution. The tabulation below gives the concentration of retardant that is represented by the several aliquot volumes of standard. Calculate the concentration of acracid red in each standard from the known composition of the specific retardant.

Volume of standard	Concentration
mL	*mg/100 mL*
0.25	0.050
.50	.100
.75	.150
1.00	.200
1.25	.250

III. Preparation of Sample (Liquid Concentrate)

A. Weigh 5 g of the sample (to ±0.01 g) and dilute it with distilled water to a total of 25.0 mL volume. Stir the mixture and centrifuge it.

B. Dilute 1.00 mL of the clear supernate to 100.0 mL in a volumetric flask. Mix the solution thoroughly.

C. Measure the absorbance of the solution at 510 nm and determine the corresponding analyte concentration from the standard curve.

D. Calculate the composition of the original material:

$$\text{Wt\%acracid red} = (2.500)\frac{\text{analyte conc.}}{\text{mass sample}}$$

IV. Preparation of Sample (Retardant at Use Level)

A. Centrifuge or filter a portion of the specimen.

B. Follow parts B and C in section III, above.

C. Calculate the composition of the original material:

$$\text{Wt\%acracid red} = (0.100)\frac{\text{analyte conc.}}{\text{density of specimen}}$$

Colorimetric Determination of Acid Violet 7 Dye (Keyacid Red 6B)[9]

Fire retardants containing acid violet 7 dye as a coloring agent are analyzed using the absorbance characteristics of the dye. The absorbance due to the dye is measured by subtracting the continuous "baseline" absorbance of the rest of the retardant from the total absorbance at 525 nm.

[8]Refer to confidential disclosure sheets for proper ingredients and amounts. (Manufacturers of fire retardants are required to submit these lists of all components and their amounts prior to evaluation.)

[9]Developed by the staff of the Intermountain Fire Sciences Laboratory based on known chemical properties of the analyte substance.

I. Preparation of Standard Solutions

A. Weigh 0.500 g of the dye, dissolve it in distilled water, and transfer it into a 100-mL volumetric flask. Add water to the mark and mix.

B. Dilute exactly 5.00 mL of this solution in a 500-mL volumetric flask, yielding a solution 50 ppm in the dye.

C. Dilute aliquots of the 50-ppm solution to give standard solutions of 2.00, 5.00, and 10.00 ppm dye concentrations.

II. Preparation of Sample Solution

Weigh 20.0 g of concentrate or mixed retardant into a 100-mL volumetric flask. Fill to the mark with distilled water and mix thoroughly.

III. Measurement and Calculations

A. Set up a spectrophotometer to cover the range between 400 and 700 nm.

B. Determine the maximum absorbance above baseline of each standard at the wavelengths of maximum absorbance at about 525 nm.

C. By scanning, measure the absorbance of each sample at the wavelengths of maximum absorbance at about 525 nm.

D. Plot calibration graphs (data from part B), net absorbance vs. concentration, ppm.

E. Using the net absorbance (max A − baseline A), and the calibration graph determine the concentration of dye in each sample.

F. Calculate the wt% concentrations in the sample:

$$\text{Wt\%} = (0.0100)\ \frac{\text{ppm conc.}}{\text{sample mass}}$$

Note: This procedure can also be used for determining the concentration of tolyltriazole, used as a corrosion inhibitor (see page 20). If both ingredients are present in the formulation and if desired, the determination of dye and tolyltriazole can be performed simultaneously by adding the appropriate amounts of each to the standard solution and following the dilution steps as detailed above.

CORROSION INHIBITORS AND OTHER MINOR INGREDIENTS

Corrosion inhibitors are added to retardant formulations to minimize the corrosion of airtankers, ground application equipment, and mixing and storage facilities by the active retardant salts. Blends of several chemicals are commonly used as an inhibitor and may effectively prevent corrosion to one alloy but not to another, while the reverse may be true for another inhibitor. This section describes procedures to determine the concentration of the most commonly used corrosion inhibitors.

Many retardant formulations contain a thickening agent. Although the concentration of most thickeners can be determined analytically, the resulting physical properties such as viscosity are more important. The viscosity or other rheological property is not necessarily directly related to the concentration of the thickening component. Thus, rather than determine directly the amount of thickeners present in the retardant, the viscosity of the retardant is used as an indirect (and somewhat qualitative) determination of the thickener amount present. A Brookfield model LVF viscometer or marsh funnel[10] is commonly used for this purpose.

[10]George, Charles W.; Johnson, Cecilia W. Determining fire retardant quality in the field. Missoula, MT: U.S. Department of Agriculture, Forest Service, Intermountain Forest and Range Experiment Station, Intermountain Fire Sciences Laboratory; [in preparation].

Ultraviolet Photometric Determination of 2-Mercapto-benzothiazole[11]

The analysis of 2-MBT as an inhibitor in fire retardants is based on the UV light absorption of the inhibitor in acidic methanol solution at 323 nm. Materials that precipitate in base are removed, and a correction is made for scattering of the optical beam due to any turbidity that may remain after separation of the solids.

I. Preparation of Standard Solutions

A. Weigh out 0.1000 g of the free thiol form of the MBT, dissolve it in about 50 mL of 1.0 M NaOH, transfer the solution quantitatively into a 100-mL volumetric flask, and dilute it to the mark with distilled water. Mix the solution thoroughly.

B. Pipet 5.00 mL of the MBT solution into a 500-mL volumetric flask, dilute to the mark, and mix. This solution contains 1.00×10^{-5} g of the thiol form of MBT per milliliter.

II. Preparation of a Standard Curve

A. Pipet 2.00-, 5.00-, and 10.00-mL samples of the standard MBT solution into 25-mL volumetric flasks.

B. To each flask add about 10 mL of methyl alcohol (methanol) and 1.00 mL of glacial acetic acid.

WARNING: Use a rubber bulb; do not pipet the acid by mouth. Dilute each flask to the mark with methanol and mix thoroughly.

C. Measure the absorbance at 323 nm (scanning from 480 to 280 nm) using pure methanol as a blank or in the reference beam. The measurement must be made in silica cells. These are very expensive; obtain specific instructions before use.

D. Plot a graph of absorbance (vertical) against mass of MBT (horizontal).

III. Sample Preparation

A. Weigh accurately about 3 g of the retardant into a weighed 100-mL volumetric flask. Add 5 mL of 1.0 M NaOH, add distilled water to the mark, and mix well.

B. Filter or centrifuge enough of the solution to obtain two relatively clear 10-mL aliquots (presuming duplicates are sufficient replication). A small amount of residual turbidity is permissible.

C. Pipet a 10.00-mL aliquot of the filtrate into a 25-mL volumetric flask and add 1.0 mL of glacial acetic acid. Fill to the mark with methanol and mix.

IV. Absorbance Measurement

A. Measure the absorbance at 323 nm in silica cells, scanning from 480 to 280 nm.

B. If there is any absorbance at 450 nm, subtract that value from the absorbance at 323 nm to correct for turbidity.

V. Calculation

A. Using the corrected absorbance at 323 nm, read from the standard curve the amount of MBT contained in the final analysis solution.

B. Calculate the percent of inhibitor in the original retardant:

$$\%\text{MBT} = (1000)\ \frac{\text{MBT concentration}}{\text{mass sample}}$$

[11]Private communication with Wildfire Control Division, Monsanto Corporation, Ontario, CA.

Volumetric Determination of Dichromate[12]

The dichromate content of retardants is determined by titration with a standardized solution of ferrous ammonium sulfate. The titration mixture contains hydrochloric and phosphoric acids and (as indicator) sodium diphenylamine sulfonate. The method is accurate and reliable, but requires care in the handling of the titrant solution to prevent errors due to its reactivity with atmospheric oxygen.

I. Solution Preparation

A. 0.0100 M $K_2Cr_2O_7$.—Weigh 1.471 g of ovendried $K_2Cr_2O_7$ (1 hour at 110 °C), dissolve it in distilled water, and transfer the solution quantitatively to a 500-mL volumetric flask. Fill to the mark and mix thoroughly. If the sample weight is not exactly 1.471 g, calculate the molarity of the solution:

$$\text{Molarity } Cr_2O_7^{+2} = \frac{\text{sample weight}}{147.1}$$

B. Hydrochloric acid.—Use concentrated HCl, 11.7 M.

C. 4.87 M phosphoric acid.—Dilute 1 volume of concentrated H_3PO_4 to a total of 3 volumes. Graduated cylinders are accurate enough.

D. 0.01 M diphenylamine sulfonate.—Weigh 0.14 g of the compound and dissolve it in 50 mL of distilled water. Store the solution in a small dropper bottle.

E. 0.0500 M ferrous ammonium sulfate.—Weigh 4.9 g (to ±0.1 g) of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and dissolve it in distilled water in a 250-mL volumetric flask. Fill the flask to the mark and mix well.

F. Notes on stability of solutions:

1. $K_2Cr_2O_7$ solutions are stable indefinitely.
2. Ferrous iron solutions are degraded rapidly by contact with atmospheric O_2. To handle it successfully,
   a. Prepare a fresh batch daily.
   b. Rinse the weighed salt directly from the beaker into the volumetric flask with a fine stream of distilled water.
   c. Keep the storage vessel stoppered (ground glass stopper).
   d. Don't allow the solution to stand in the buret more than a few minutes between titrations.
   e. Don't return unused titrant from the buret to the storage vessel.

II. Standardization of the Titrant Solution

A. Prepare titration solution just before a set of samples is to be titrated. If a particular titrant solution is used during more than half of a day, it is well to repeat the standardization at the end of the day.

B. Use a 20.00- or 25.00-mL aliquot of the standard dichromate solution as a sample and follow the section headed Titration Procedure.

C. Calculation

$$\text{Molarity of } Fe^{+2} = \frac{6\ (\text{molarity of } Cr_2O_7^{-2})(\text{vol } Cr_2O_7^{-2}, \text{mL})}{\text{vol } Fe^{+2}, \text{mL}}$$

III. Sample Preparation

A. Measure 25.0 mL of the retardant and dilute it with distilled water to a total volume of 100.0 mL. Stir the mixture well.

B. Use centrifugation or filtration to remove any solids from the diluted sample. Take 25.00 mL aliquots of the clear filtrate or supernate as samples for the titration. Minor amounts of color or turbidity will not interfere.

[12]Indicator application: Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, Stanley. Quantitative chemical analysis, 4th ed., The MacMillan Co.; 1969. p. 757. Titration: p. 839.

IV. Titration Procedure

A. Rinse the buret three times with about 5 mL of the titrant (Fe^{+2}) solution; then fill it with the titrant.

B. Pipet sample aliquots into 125- or 250-mL Erlenmeyer flasks and add distilled water to bring the volume to about 25 mL.

C. Add to each sample 1.0 mL of the HCl solution, 1.0 mL of the H_3PO_4 solution, and 6 drops of the diphenylamine sulfonate indicator solution.

D. Titrate the sample with steady swirling of the flask. At the beginning, the sample will be a dark brownish color. After some of the dichromate has been reduced, the sample will look purple. The end-point change is quite abrupt, from the purple color to a bright green. There is little warning; the purple will pale slightly a drop or two ahead of the color change.

E. Calculation

$$\%Na_2Cr_2O_7 \cdot 2H_2O = (\text{titration volume, mL})(\text{molarity } Fe^{+2}) \frac{0.795}{d}$$

where

d is the specific gravity of the original sample.

Volumetric Determination of Thiosulfate[13]

The analysis for thiosulfate inhibitor in fire retardants is based on the iodometric titration of iodine with thiosulfate. An excess of iodide is added to the sample; then an accurately known amount of iodate is added, which produces an exactly equivalent amount of elemental iodine:

$$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Enough iodate is added to generate an excess of iodine over that needed to react with the thiosulfate in the sample.

$$I_2 + 2S_2O_3^{-2} \rightarrow 2I^- + S_4O_6^{-2}$$

The excess iodine is then titrated with a standard solution of sodium thiosulfate. The presence of traces of the retardant-coloring material does not interfere because the blue color of the starch-iodine complex is quite intense. Each titration sample should be 1.5 M in sulfuric acid.

I. Solution Preparation

A. 6 M sulfuric acid.—Slowly, with continuous stirring, pour 83 mL of concentrated H_2SO_4 into 150 mL of distilled water contained in a 500-mL Erlenmeyer flask. Add enough more water to bring the total volume to 250 mL. Invert a beaker over the flask neck and stand it under a cold water tap to cool the solution.

B. 0.008 M sodium iodide.—Weigh 0.60 g of NaI (or 0.66 g KI), dissolve it in distilled water, and dilute the solution to about 500 mL. These measurements need not be highly accurate.

C. 0.00600 N potassium iodate.—Weigh accurately about 0.13 g of KIO_3, dissolve it in distilled water in a 500-mL volumetric flask. Fill to the mark and mix well. Calculate the normality of the solution:

$$N = \frac{\text{exact mass } KIO_3}{17.84} \text{ equiv/liter}$$

D. 0.01 N sodium thiosulfate.—In a 1-liter Erlenmeyer flask, boil about 700 mL of distilled water for 5 minutes; then cool it under cold running water with a beaker over the mouth of the flask. This kills sulfur bacteria that would otherwise grow in the solution. Weigh 1.24 g of $Na_2S_2O_3 \cdot 5H_2O$, dissolve it in

[13]Kolthoff, I. M.; Sandel, E. B.; Meehan, E. J.; Bruckenstein, Stanley. Quantitative clinical analysis, 4th ed., The MacMillan Co.; 1969: 846-850.

some of the boiled water, and dilute it to about 500 mL. These volumes need not be highly exact.

E. Starch indicator.—Weigh about 0.5 g of soluble potato starch and triturate it with a few drops of distilled water to form a thin paste; then rinse the paste into a storage bottle, diluting it to about 100 mL.

II. Standardization of $Na_2S_2O_3$ Solution

In this procedure and the sample analysis itself, the iodide and iodate solutions are always used together in equal volumes. In doing this, the iodide will always be in excess and the accuracy of its volume measurement is not critical. The quantitative calculation of results, however, rests on the exact amount of iodate used.

A. Fill the buret with the $Na_2S_2O_3$ solution.

B. Into a 125-mL Erlenmeyer flask, pipet exactly 20.00 mL of the IO_3^- solution. Add about 30 mL of distilled water and 10 mL of 6 M H_2SO_4.

C. Add about 20 mL of the NaI solution; this will cause a deep brown color due to elemental iodine, present as I_3^-.

D. Titrate the sample immediately (I_2 vapor can be lost) with thiosulfate until the color is almost gone; only a faint yellow should remain.

E. Add 2 or 3 mL of the starch solution. The sample solution will become deep blue.

F. Continue to add $S_2O_3^{-2}$ titrant until the last drop destroys the last of the blue color.

G. Calculate the normality of the $S_2O_3^{-2}$ solution:

$$N = \frac{(\text{vol } IO_3^- \text{ used})\,(\text{normality } IO_3^-)}{\text{vol } S_2O_3^{-2} \text{ titrant}}$$

H. Repeat A through G until adequate reproducibility is demonstrated.

III. Retardant Analysis

A. Measure accurately a 25-g sample of the retardant into a 250-mL volumetric flask. Fill to the mark and mix well.

B. Centrifuge portions of the diluted sample until 100 mL of (relatively) clear supernate have been accumulated. A 100-mL graduated cylinder is sufficiently accurate.

C. Pour the 100-mL sample into a 250-mL Erlenmeyer flask; then add 30 mL 6 M H_2SO_4 and 10 mL 0.008 M NaI.

D. Swirl the sample; then add 10.00 mL (accurately measured) of the standard KIO_3.

E. Add 2 or 3 mL starch solution. The concentration of I_3^- is much lower than in the standardization and the residual color of the retardant complicates seeing the yellow of the last of the I_3^-, so the starch can be added before beginning the titration.

F. Titrate to an end point indicated by the fading of the dark bluish cast of the starch-I_2 back to the color possessed by the centrifugation supernate.

IV. Calculation

$$\%Na_2S_2O_3 \cdot 5H_2O = (31.03)\,\frac{(V_I)(N_I) - (V_S)(N_S)}{\text{mass sample}}$$

where

V_I and N_I are the volume and normality of the KIO_3 solution (added reagent).

V_S and N_S are the volume and normality of the $Na_2S_2O_3$ solution (titrant).

Volumetric Determination of Ferrocyanide[14]

The ferrocyanide ion, $Fe(CN)_6^{-4}$, is oxidized by adding a standard solution of either potassium dichromate or potassium permanganate. The end point can be detected by means of a polarized pair of platinum electrodes (either reagent) or by the appearance of the first excess of reagent (permanganate color).

The inhibitor, sodium ferrocyanide (yellow prussiate of soda, YPS), has been analyzed in this laboratory and found to have between 7.5 and 8.0 moles of water per mole of compound. (Matheson, Coleman and Bell, Reagent: 7.73; commercial grade from a retardant manufacturer: 7.56.) The effective formula weight is thus about 440.

I. Preparation of Solutions

A. 0.005 N potassium dichromate.—Weigh 0.2450 g of dry $K_2Cr_2O_7$ (1 hour at 110 °C), dissolve in distilled water, and dilute to exactly 1 liter (volumetric flask). Calculate the exact normality:

$$N = 0.02039 \text{ (mass } K_2Cr_2O_7)$$

The solution is stable indefinitely.

B. 0.005 N potassium permanganate.— Weigh about 0.16 g of $KMnO_4$ in a 50-mL beaker. Dissolve it in successive portions of distilled water, crushing the crystals with a glass rod. Decant the solutions into a 1-liter bottle (glass), continuing until the last crystals dissolve; do not transfer any solid $KMnO_4$ into the bottle. Dilute to about 1 liter and stir. Measurements need not be exact because the solution will be standardized.

C. 0.012 N oxalic acid.—Weigh about 0.4 g (to ±0.0001 g) of $C_2H_2O_4 \cdot 2H_2O$. Dissolve it in distilled water and dilute to 500.0 mL in a volumetric flask. Calculate the normality:

$$N = 0.03173 \text{ (mass sample)}$$

II. Standardization of the $KMnO_4$ Solution

A. Fill a buret with the $KMnO_4$ solution.

B. Pipet exactly 10.00 mL of the $H_2C_2O_4$ solution into a 100-mL beaker and add 6 mL of 6 N H_2SO_4 (3 M); stir continually with a stirbar and magnetic stirrer.

C. Add about 10 mL of the titrant to the beaker (a total of 25 to 30 mL will be required) and warm the beaker over a low Bunsen flame or on a hot plate until the $KMnO_4$ color disappears. The solution will then be at about 60 °C.

D. Continue the titration to the first tinge of color due to excess $KMnO_4$.

E. Repeat until consistent results are obtained, average these values, and calculate the normality of the titrant solution:

$$N = \frac{(\text{normality } H_2C_2O_4)(\text{volume } H_2C_2O_4)}{\text{volume } KMnO_4}$$

F. *NOTE:* The $KMnO_4$ solution may remain stable for some time (days; maybe a week), but it is subject to decomposition. Protect the solution from any contact with organic material (wood, paper, etc.), and store in glass-stoppered bottles. A sample of $H_2C_2O_4$ should be titrated daily. The oxalic acid is stable for long periods of time (months).

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[14]Permanganate standardization: Kolthoff, I. M.; Sandel, E. B; Meehan, E. J.; Bruckenstein, Stanley. Quantitative chemical analysis, 4th ed., The MacMillan Co.; 1969: 825-827. Analysis developed by Intermountain Fire Sciences Laboratory staff based on known chemical properties of the analyte substance.

III. Analysis of Retardants

Gum-thickened retardants must be treated with enzyme to reduce viscosity and then centrifuged prior to analysis.[15] If the specimen is uncolored or can be filtered or centrifuged to give a clear, lightly colored solution, the appearance of the color of excess $KMnO_4$ can be used for end-point detection. In any case, biamperometric end-point detection can be used for any type of retardant and with either $K_2Cr_2O_7$ or $KMnO_4$ reagent.

A. $KMnO_4$ titration

1. Measure accurately (mass or volume) a sample estimated to contain 40 to 60 mg of sodium ferrocyanide. Add distilled water, if necessary, to give a total volume of about 20 mL in a 100-mL beaker.

2. Add 10 mL of 6 N H_2SO_4 and stir continuously using a magnetic stirrer and stirbar.

3. Titrate to the first tinge of $KMnO_4$ color. If the sample is originally yellow in color, the end point (more difficult to detect) will be the onset of an orange hue.

4. Calculate the inhibitor content:

$$\%Na_4Fe(CN)_6 \bullet H_2O = (44.0)\ \frac{(\text{volume } KMnO_4,\ \text{mL})(\text{normality } KMnO_4)}{\text{mass sample}}$$

B. Biamperometric titration

The assembly and adjustment of the electronic apparatus are described in a note to this procedure.

1. Measure accurately a sample that weighs between 5 and 10 g into a 100-mL beaker. Add enough distilled water to cover a stirbar and the platinum electrodes. This will be about 50 mL.

2. Position the electrodes and the buret, and add 10 mL of 6 N H_2SO_4, with the stirrer running. Immediately add 2 or 3 mL of titrant.

NOTE: At this point, the electrode system should indicate a significant signal. Under correct conditions, the signal (current between polarized Pt electrodes) will fall to zero as the iron (II) is all oxidized. Beyond the end point, the current will increase again (standardization with oxalate) or stay near zero (usual with thickened retardants).

3. After each addition of titrant, note the position of a sweep-second or digital timer. When 30 seconds have elapsed, read and record the electrode system signal and the corresponding buret level reading.

4. Add titrant, 1 to 4 mL at a time, reading volumes to ± 0.01 mL. Continue readings at least 10 mL beyond the end point. It is necessary that data beyond the end point be sufficient to define a straight line.

NOTE: With some retardant systems, the electrodes become desensitized by an electrodeposited film. This is revealed by a low (or zero) signal at the beginning of a run. To correct this, immerse the electrodes in 1 M HNO_3, reverse the polarity of the applied potential, and increase that potential to 2 or 3 volts. Allow the resulting electrolysis to run for up to 1 minute. Rinse off the nitric acid and resume the analysis.

5. Plot the data on good quality graph paper (signal vertical, volume horizontal), draw straight lines connecting the last few data points before and after the end point, and identify the end point volume—the intersection of those lines.

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[15]George, Charles W.; Johnson, Cecilia W. Determining fire retardant quality in the field. Missoula, MT: U.S. Department of Agriculture, Forest Service, Intermountain Forest and Range Experiment Station, Intermountain Fire Sciences Laboratory; [in preparation].

6. Calculate the inhibitor content using the equation above (III.A.4).

NOTE: Adjustment of Instrumentation for Ferrocyanide Determination

For the biamperometric titration, this lab uses Princeton Applied Research Corp. equipment, model 173 - potentiostat/galvanosat, model 376 - logarithmic current converter, model 178 - electrometer probe, and Orion Research model 701A pH meter. Other equipment may be suitable but will require appropriate modification of the setup described below. Leave the PAR Model 175 programmer turned off. Disconnect the 175-output cable from the Model 173 potentiostat external signal input jack. Disconnect the cable from the Number 1 output jack on the Model 376 converter and in its place connect a cable that is designed to carry the output signal from the 376 to the input of an Orion Research model 701A pH meter (or comparable readout). This cable must have tight, solidly soldered connections.

The external cell cable bears three alligator-clip connectors. The red and green leads should be connected to the leads of a pair of platinum wire electrodes. These electrodes are designed for polarized-pair biamperometric end-point detection, and are made of two pieces of Pt wire, about 18 gauge, sealed into a single glass probe and spaced about 5 mm apart. The third lead (black) is not used.

The electrometer probe clip should be connected directly to the red lead alligator clip. Do not use the noise filter.

Set the Applied Potential A Channel to 0.400 volt, negative polarity.

Set the Operative Mode at Control E, external cell.

Set the meter switch to "current."

On the 376 converter, set the filter to 10 ms, the IR compensation to "off," and use the range decade control as needed to obtain signal readout of sufficient number of digits. Usually the 1 mA setting is appropriate.

Volumetric Determination of Thiocyanate[16]

The oxidation of SCN^- in acid medium (1.5 N H_2SO_4) by permanganate involves consumption of about six equivalents of MnO_4^- per mole of SCN^-. The exact empirical ratio is 5.84 eq/mole, and this number is used in calculating the analytical results. This is consistent with the reaction:

$$5\ SCN^- + 6\ MnO_4^- + 8H^+ \rightarrow 6\ Mn^{+2} + 5\ SO_4^{-2} + 5\ CN^- + 4\ H_2O$$

The chemical system will not respond to electrochemical (biamperometric) detection. Refer to the notes on permanganate usage in the section on the determination of ferrocyanide.

I. Solution Preparation

Follow the instructions in the ferrocyanide procedure, parts I.B and I.C, except that in both cases, use 10 times as much of the chemical (1.6 g $KMnO_4$ and 4.0 g $H_2C_2O_4$).

II. Standardization of the $KMnO_4$

Follow the procedures in the ferrocyanide analysis, part II.

III. Sample Preparation

A. Measure accurately about 5 g of the retardant into a 100-mL volumetric flask. Dilute to the mark and mix thoroughly.

B. Centrifuge about 20 mL of this solution, and pipet 10.00 mL of the supernate into a 100-mL beaker.

C. Add water to give a total volume of about 20 mL, add 10 mL of 6 N H_2SO_4, and provide a magstir and stirbar.

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[16]Analysis developed by Intermountain Fire Sciences Laboratory staff based on known chemical properties of the analyte substances (substance).

D. Titrate to the first tinge of $KMnO_4$ color, or until an originally yellow sample solution first develops an orange hue.

E. Calculate the inhibitor content:

$$\%NH_4SCN = (13.04)\ \frac{(\text{volume } MnO_4^-,\ \text{mL})(\text{normality } MnO_4^-)}{\text{mass sample}}$$

Colorimetric Determination of Tolyltriazole[17]

The absorbance due to the inhibitor is measured by subtracting the continuous "baseline" absorbance of the thickener from the total absorbance at 274 nm. Mercaptobenzothiazole will interfere with this analysis.

I. Preparation of Standard Solutions

A. Weigh 8.0 g of the commercially available 50 percent solution of tolyltriazole and transfer it into a 100-mL volumetric flask. Add water to the mark and mix.

B. Dilute exactly 5.00 mL of this solution in a 500-mL volumetric flask, yielding a solution 400 ppm in the inhibitor.

C. Dilute aliquots of the 400-ppm solution to give standard solutions of 16.0, 40.0, and 80.0 ppm concentrations of inhibitor.

II. Preparation of Sample Solution

Weigh 20.0 g of retardant into a 100-mL volumetric flask. Fill to the mark with distilled water and mix thoroughly.

III. Measurement and Calculations

A. Set up a spectrophotometer to cover the range between 200 and 300 nm.

B. Determine the maximum absorbance above baseline of each standard at the wavelength of maximum absorbance at about 274 nm.

C. By scanning, measure the absorbance of each sample at the wavelength of maximum absorbance at about 274 nm.

D. Plot calibration graph (data from part B), net absorbance vs. concentration, ppm.

E. Using the net absorbance (max A − baseline A), and the calibration graph determine the concentration of inhibitor in each sample.

F. Calculate the wt% concentrations in the sample:

$$\text{Wt\%} = (0.0100)\ \frac{\text{analyte concentration}}{\text{sample mass}}$$

NOTE: This procedure can also be used for determining the concentration of acid 7 violet dye, used as a coloring agent (see page 00). If both ingredients are present in the formulation and if desired, the determination of dye and tolyltriazole can be performed simultaneously by adding the appropriate amounts of each to the standard solution and following the dilution steps as detailed above.

TRACE METAL CONCENTRATIONS[18]

Certain retardant products employ a fertilizer grade of concentrated ammonium polyphosphate solution as the ingredient that imparts long-term effectiveness to the mixture. Because some sources of this material are known to be more corrosive to metals than others, procurement specifications may require a particular brand of the liquid concentrate (LC).

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[17]This method was developed by the staff at the Intermountain Fire Sciences Laboratory based on known chemical properties of the analyte substance.

[18]This method was developed by the staff of the Intermountain Fire Sciences Laboratory.

A method of monitoring compliance with such a requirement can be based on the fact that phosphate products, originating from mineral deposits, contain a suite of trace elements whose identities and concentrations can constitute a signature characteristic of the source. Chemical analyses for six elements have been performed on LC specimens from six different suppliers (table 1).[19] As a trial to test the concept, 16 retardant samples from 12 different airtanker bases have been analyzed for the same six elements—cadmium, chromium, copper, manganese, nickel, and zinc (table 2). Each of these samples is supposed to contain LC from the same supplier.

For each element in each sample, the quantity R has been calculated, where

$$R = \frac{|(\text{sample concentrate}) - (\text{reference concentrate})|}{(\text{reference concentrate})}$$

and the reference concentration in each case is the concentration of the element concerned in that particular LC which is supposed to be in the sample. Thus, when for each sample the values of R are summed, the sum should be much smaller for a "correct composition" case than for one in which another brand of LC was employed.

Among the 16 samples were two which had been diluted to use level (4:1) before sampling. These two had much higher concentrations of copper than any of the others. It is possible they were contaminated by corroded processing equipment, but the manganese values were also discordant. (See specimens 3 and 15 in table 2.)

The results of computations are shown in tables 3 through 8. Some analytical results were listed as "less than" certain values. These were entered into computer program data files without the qualifier. Thus, "<0.1" was treated as 0.1.

The 16 field samples were of material that should have been formulated using LC from source A. On the basis of the results shown in table 3, and presuming that most of them were indeed in compliance with specifications, it appears that if the sum of R values is less than about 5, compliance is indicated. The high value of Cr in sample 4 is not so easily explained as the Cu in numbers 3 and 15, and the discrepant Mn values encourage the conclusion that all three may contain LC from a source or sources other than source A.

Tables 4 through 8 illustrate the results of using other source data as the reference. These point up the first of two weaknesses of the system. Since the metal concentrations among the six source materials show strong variations, a good computation system should show large "flags" when a field sample is referred to a source LC other than the one actually used. Tables 4, 5, 6, and 8 do not bear this out.

The second weakness results from the way the function R interacts with real data. If the reference concentration is quite small, then the R for that element will be overpoweringly large, even when the actual concentration in the sample is not alarmingly great. Also, if a reference concentration is relatively large, it tends to understate the size of its R compared to those of the other metals.

Simple relationships for the data pairs, other than that shown, have been sought, but without success in eliminating the difficulties referred to above. The technique could have important and useful applications in quality assurance. Without more development, it cannot be considered fully proved. A definite need exists to examine retardant concentrates formulated using known specimens of several of the available polyphosphate products.

[19]All tables referred to in this section can be found in the appendix.

RECOVERY OF RETARDANT FROM VEGETATION/DUFF/ SOIL AND DETERMINATION OF RATE OF COVERAGE[20]

To evaluate the effectiveness of retardant chemicals in the field under operational conditions, it is necessary to know the amount of retardant chemical applied. Determinations have been made successfully in the past of samples collected from field areas where applications from airtankers or ground equipment have been made on actual fires. Usually 1 ft^2 of ground surface has been cleared, placing all material that might be coated with retardant into a plastic bag. The objective of the procedure is the measurement of the rate of coverage of the retardant, commonly reported in gallons per 100 ft^2.

The laboratory procedure uses a leaching step (dilute hydrochloric acid), followed by filtration; then by analysis for ammonium or phosphate ion.

I. Specimen Leach Procedure

A. Transfer the specimen (total sample bag contents) into a beaker large enough (2 liters) to allow complete immersion of the material.

B. Rinse the inside of the sample bag with three successive 100-mL (approximately) portions of distilled water, pouring them into the beaker.

C. Add more distilled water such that:

1. The beaker is not more than two-thirds full;
2. The specimen material is fully covered.

D. Add 5 mL concentrated hydrochloric acid per liter of water.

E. Stir occasionally; let stand overnight.

II. Filtration

A. Use large porcelain Buchner funnels with filter paper circles to fit.

B. Decant, retaining as much of the solids in the beaker as possible. Rinse the residue twice, passing the rinses through the filter.

C. Transfer the filtrate quantitatively into a volumetric flask, dilute to the mark, and stir. Use a 1-liter flask, if possible; larger, if necessary.

III. Analytical Samples

A. Both the ammonium (page 2) and phosphate (page 4) methods are based on starting with a 0.1-g sample of retardant. The equation below indicates the aliquot volume of filtrate necessary to constitute a sample of the correct size for:

1. Step III.A of the phosphate method.
2. Direct insertion into the Kjeldahl apparatus for the ammonia determination.

$$\text{Volume} = (0.179)\frac{\text{flask volume, II.C, above}}{\text{area sampled, in}^2}$$

Example: 1 ft^2 area; 2-liter flask:

$$\text{Volume} = (0.179)\frac{2{,}000}{144} = 2.49 \text{ mL}$$

NOTES:

1. Increase this volume to the nearest whole milliliter.
2. This equation is based on a presumed coverage rate of 2 gallons per 100 ft^2.

[20]This method was developed by the staff at the Intermountain Fire Sciences Laboratory.

IV. Calculations

A. Ammonia analysis

The data will include:

- total volume of leach solution, V_L, mL
- volume of aliquot taken for Kjeldahl process, V_A, mL
- concentration of the standard acid titrant, N_H
- volume of titrant acid used, V_H, mL
- size of the area sampled in the field, A, in^2

The rate of coverage, gallons retardant/100 ft^2

$$= \frac{V_H\, N_H\, V_L\, FW(144)(100)}{V_A\, A\, (1{,}000)nF_S(453)d}$$

$$= (0.03179)\, \frac{V_H\, N_H\, V_L\, FW}{V_A AnF_S\, d}$$

where

FW = formula weight of the salt used

n = number of NH_4^+

FS = fractional salt composition of retardant; e.g.:

if a retardant is 15.6 percent AS; thus $F_S = 0.156$

d = density of retardant, lb/gal.

B. Phosphate analysis

The data will include:

- total volume of the leach solution, V_L, mL
- volume of aliquot taken for phosphate analysis, V_A, mL
- analytical result, concentration of P_2O_5 in final sample solution, ppm
- size of area sampled in the field, A, in^2.

The rate of coverage, gallons retardant/100 ft^2

$$= \frac{ppm(1{,}000)(2)FW(144)(100)}{(10^6)(142.04)(453)\, V_A F_S A\, d}$$

$$= \frac{(0.0004479)(ppm)}{V_A\, F_S\, A\, d}$$

where

F_S = fractional salt composition of retardant; e.g.: if a retardant is 10.6 percent DAP; then $F_S = 0.106$

d = density of retardant, lb/gal

FW = formula weight of the phosphate salt used

DAP = 132.1, MAP = 115.1

APPENDIX

Table 1.—Trace metal concentrations in commercial sources of liquid ammonium polyphosphate

Source	Concentrations					
	Cd	Cr	Cu	Mn	Ni	Zn
	ppm					
A	1	37	9	207	26	78
B	59	283	3	319	72	719
C	18	370	24	46	40	432
D	5	450	33	73	35	321
E	11	110	3	25	4	207
F	43	251	46	643	25	383

Table 2.—Trace metal concentrations in concentrated fire retardant mixtures

Sample No.	Concentrations					
	Cd	Cr	Cu	Mn	Ni	Zn
	ppm					
1	0.1	31	4	140	11	32
2	.1	51	4	86	13	71
3	.1	59	202	223	32	150
4	.1	486	7	151	12	53
5	.1	35	6	135	10	50
6	.1	38	5	89	9	39
7	.1	41	9	174	13	52
8	.1	40	8	146	12	55
9	.1	38	5	146	11	50
10	.1	37	5	129	11	49
11	.1	37	6	141	16	54
12	.1	39	5	127	12	49
13	.1	41	5	124	9	45
14	1.	33	38	124	17	72
15	1.	38	190	5	1	38
16	1.	36	64	128	7	82

Table 3.—Computations using source A (Allied) as the reference

Sample No.	R^1						Sum of R values
	Cd	Cr	Cu	Mn	Ni	Zn	
1	0.90	0.16	0.56	0.32	0.58	0.59	3.11
2	.90	.38	.56	.58	.50	.09	3.01
3	.90	.59	21.44	.08	.23	.92	24.17
4	.90	11.65	.22	.27	.54	.32	13.90
5	.90	.05	.33	.35	.62	.36	2.61
6	.90	.03	.44	.57	.65	.50	3.10
7	.90	.11	.00	.16	.50	.33	2.00
8	.90	.08	.11	.29	.54	.29	2.22
9	.90	.03	.44	.29	.58	.36	2.60
10	.90	.00	.44	.38	.58	.37	2.67
11	.90	.00	.33	.32	.38	.31	2.24
12	.90	.05	.44	.39	.54	.37	2.70
13	.90	.11	.44	.40	.65	.42	2.93
14	.00	.11	3.22	.40	.35	.08	4.15
15	.00	.03	20.11	.98	.96	.51	22.59
16	.00	.03	6.11	.38	.73	.05	7.30

$$^1R = \frac{|(\text{Sample concentration}) - (\text{reference concentration})|}{\text{reference concentration}}$$

Table 4.—Computations using source B (Simplot) as the reference

Sample No.	R^1						Sum of R values
	Cd	Cr	Cu	Mn	Ni	Zn	
1	1.00	0.89	0.33	0.56	0.85	0.96	4.59
2	1.00	.82	.33	.73	.82	.90	4.60
3	1.00	.79	66.33	.30	.56	.79	69.77
4	1.00	.65	1.33	.53	.83	.93	5.27
5	1.00	.88	1.00	.58	.86	.93	5.24
6	1.00	.87	.67	.72	.88	.95	5.07
7	1.00	.86	2.00	.45	.82	.93	6.06
8	1.00	.86	1.67	.54	.83	.92	5.82
9	1.00	.87	.67	.54	.85	.93	4.85
10	1.00	.87	.67	.60	.85	.93	4.91
11	1.00	.87	1.00	.56	.78	.92	5.13
12	1.00	.86	.67	.60	.83	.93	4.89
13	1.00	.86	.67	.61	.88	.94	4.94
14	.98	.88	11.67	.61	.76	.90	15.81
15	.98	.87	62.33	.98	.99	.95	67.10
16	.98	.87	20.33	.60	.90	.89	24.58

$$^1R = \frac{|(\text{Sample concentration}) - (\text{reference concentration})|}{\text{reference concentration}}$$

Table 5.—Computations using source C (Stauffer) as the reference

Sample No.	R^1						Sum of R values
	Cd	Cr	Cu	Mn	Ni	Zn	
1	0.99	0.92	0.83	2.04	0.73	0.93	6.44
2	.99	.86	.83	.87	.68	.84	5.07
3	.99	.84	7.42	3.85	.20	.65	13.95
4	.99	.26	.71	2.28	.70	.88	5.83
5	.99	.91	.75	1.93	.75	.88	6.22
6	.99	.90	.79	.93	.78	.91	5.30
7	.99	.89	.63	2.78	.68	.88	6.85
8	.99	.89	.67	2.17	.70	.87	6.30
9	.99	.90	.79	2.17	.73	.88	6.47
10	.99	.90	.79	1.80	.73	.89	6.10
11	.99	.90	.75	2.07	.60	.88	6.18
12	.99	.89	.79	1.76	.70	.89	6.03
13	.99	.89	.79	1.70	.78	.90	6.04
14	.94	.91	.58	1.70	.58	.83	5.54
15	.94	.90	6.92	.89	.98	.91	11.54
16	.94	.90	1.67	1.78	.83	.81	6.93

$$^1R = \frac{|(\text{Sample concentration}) - (\text{reference concentration})|}{\text{reference concentration}}$$

Table 6.—Computations using source D (Cominco) as the reference

Sample No.	R[1] Cd	Cr	Cu	Mn	Ni	Zn	Sum of R values
1	0.98	0.93	0.88	0.92	0.69	0.90	5.29
2	.98	.89	.88	.18	.63	.78	4.33
3	.98	.87	5.12	2.05	.09	.53	9.64
4	.98	.04	.79	1.07	.66	.83	4.37
5	.98	.92	.82	.85	.71	.84	5.13
6	.98	.92	.85	.22	.74	.88	4.58
7	.98	.91	.73	1.38	.63	.84	5.47
8	.98	.91	.76	1.00	.66	.83	5.13
9	.98	.92	.85	1.00	.69	.84	5.27
10	.98	.92	.85	.77	.69	.85	5.05
11	.98	.92	.82	.93	.54	.83	5.02
12	.98	.91	.85	.74	.66	.85	4.99
13	.98	.91	.85	.70	.74	.86	5.04
14	.80	.93	.15	.70	.51	.78	3.87
15	.80	.92	4.76	.93	.97	.88	9.26
16	.80	.92	.94	.75	.80	.74	4.96

[1]$R = \frac{|(\text{Sample concentration}) - (\text{reference concentration})|}{\text{reference concentration}}$

Table 7.—Computations using source E (Texas Gulf) as the reference

Sample No.	R[1] Cd	Cr	Cu	Mn	Ni	Zn	Sum of R values
1	0.99	0.72	0.33	4.60	1.75	0.85	9.24
2	.99	.54	.33	2.44	2.25	.66	7.21
3	.99	.46	66.33	7.92	7.00	.28	82.98
4	.99	3.25	1.33	5.04	2.00	.74	13.36
5	.99	.68	1.00	4.40	1.50	.76	9.33
6	.99	.65	.67	2.56	1.25	.81	6.93
7	.99	.63	2.00	5.96	2.25	.75	12.58
8	.99	.64	1.67	4.84	2.00	.73	10.87
9	.99	.65	.67	4.84	1.75	.76	9.66
10	.99	.66	.67	4.16	1.75	.76	8.99
11	.99	.66	1.00	4.64	3.00	.74	11.03
12	.99	.65	.67	4.08	2.00	.76	9.15
13	.99	.63	.67	3.96	1.25	.78	8.28
14	.91	.70	11.67	3.96	3.25	.65	21.14
15	.91	.65	62.33	.80	.75	.82	66.26
16	.91	.67	20.33	4.12	.75	.60	27.39

[1]$R = \frac{|(\text{Sample concentration}) - (\text{reference concentration})|}{\text{reference concentration}}$

Table 8.—Computations using source F (Wolfkill) as the reference

Sample No.	R[1] Cd	Cr	Cu	Mn	Ni	Zn	Sum of R values
1	1.00	0.88	0.91	0.78	0.56	0.92	5.05
2	1.00	.80	.91	.87	.48	.81	4.87
3	1.00	.76	3.39	.65	.28	.61	6.70
4	1.00	.86	.85	.77	.52	.86	4.86
5	1.00	.86	.87	.79	.60	.87	4.99
6	1.00	.85	.89	.86	.64	.90	5.14
7	1.00	.84	.80	.73	.48	.86	4.71
8	1.00	.84	.83	.77	.52	.86	4.81
9	1.00	.85	.89	.77	.56	.87	4.94
10	1.00	.85	.89	.80	.56	.87	4.97
11	1.00	.85	.87	.78	.36	.86	4.72
12	1.00	.84	.89	.80	.52	.87	4.93
13	1.00	.84	.89	.81	.64	.88	5.06
14	.98	.87	.17	.81	.32	.81	3.96
15	.98	.85	3.13	.99	.96	.90	7.81
16	.98	.86	.39	.80	.72	.79	4.53

[1]$R = \frac{|(\text{Sample concentration}) - (\text{reference concentration})|}{\text{reference concentration}}$

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Van Meter, Wayne P.; George, Charles W.; Johnson, Cecilia W. Chemical analysis procedures for forest fire constituents. General Technical Report INT-181. Ogden, UT: U.S. Department of Agriculture, Forest Service, Intermountain Forest and Range Experiment Station; 1985. 25p.

Describes procedures used at the Intermountain Fire Sciences Laboratory for determining components of fire retardant mixtures, including inorganic salts, coloring agents, and spoilage and corrosion inhibitors. Includes measurement of field application rates.

KEYWORDS: chemical analysis, fire retardants

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